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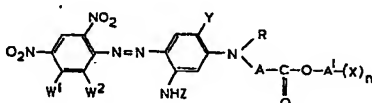


(54) MONOAZO DYESTUFFS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to water-insoluble monoazo dyestuffs which are valuable for colouring synthetic textile materials, in particular aromatic polyester textile materials.

According to the invention there are provided the water-insoluble monoazo dyestuffs, free from sulphonic and carboxylic acid groups, which are of the formula:—



wherein W<sup>1</sup> is hydrogen, chlorine, bromine, cyano or an acylamino group of the formula NHZ<sup>1</sup> and W<sup>2</sup> is hydrogen, chlorine, bromine, cyano or nitro, provided that one, but not both, of W<sup>1</sup> and W<sup>2</sup> is hydrogen; Z<sup>1</sup> and Z<sup>2</sup> each independently represents an acyl group of the formula —COV or —SO<sub>2</sub>U; V is an amino group or a lower alkyl, lower alkoxy, phenyl or phenoxy radical which can contain substituents; U is a lower alkyl or phenyl radical which can contain substituents; Y is hydrogen, lower alkyl or lower alkoxy; R is lower alkyl, hydroxy lower alkyl, lower alkoxy lower alkyl, acyl lower alkyl,  $\beta$ -phenoxyethyl,  $\beta$ -acetoxyethyl,  $\beta$ -( $\beta'$ -

acetoxyethoxy)ethyl,  $\gamma$ -chloro- $\beta$ -hydropropyl,  $\beta$ -ethoxycarboxyethyl or optionally substituted phenyl;

A is an alkylene radical containing from 1 to 6 carbon atoms having not more than two carbon atoms between the nitrogen atom N and the carbonyl group;

n is 1 or 2, and A' represents a di- or tri-valent alkane radical, depending on the value of n, containing up to 4 carbon atoms;

and X is cyano, lower alkoxy, optionally substituted phenoxy, hydroxy, chlorine, bromine, lower alkoxy carbonyl, optionally substituted phenoxy carbonyl, carbamoyl, optionally substituted N-phenylcarbamoyl, N-lower alkyl or N:N-di lower alkyl carbamoyl, amino, optionally substituted anilino, N-lower alkylamino, N:N-di lower alkylamino, lower alkylsulphonyl, optionally substituted phenylsulphonyl or a radical of the formula U.CO—, U.COO or UCONH—.

Throughout this Specification the terms "lower alkyl" and "lower alkoxy" are used to denote alkyl and alkoxy radical respectively containing from 1 to 4 carbon atoms.

As examples of the lower alkyl radicals represented by R, U, V and Y there may be mentioned methyl, ethyl, n-propyl and n-butyl, and as examples of the lower alkoxy radicals represented by V and Y there may be mentioned n-propoxy, n-butoxy and preferably ethoxy and methoxy. As examples of the substituted lower alkyl radicals represented by U, V and R there may be mentioned hydroxy lower alkyl such as  $\beta$ -hydroxyethyl, lower alkoxy alkyl such as  $\beta$ -(methoxy or ethoxy)ethyl and  $\gamma$ -methoxypropyl and aryl lower alkyl such as benzyl and  $\beta$ -phenylethyl. As examples of the substituted phenyl radicals represented by U, V and R there may be

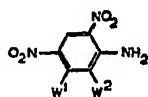
mentioned tolyl, anisyl, chlorophenyl and bromophenyl. As examples of the substituted phenoxy radicals represented by V there may be mentioned chlorophenoxy and bromophenoxy.

It is however, preferred and Z and Z' each independently represent a lower alkyl carbonyl radical. It is also preferred that R represents a lower alkyl radical.

- 10 Examples of the radicals represented by X include lower alkoxy such as methoxy and ethoxy, optionally substituted phenoxy such as phenoxy, tolyloxy and methoxyphenoxy, lower alkoxy-carbonyl such as methoxycarbonyl and ethoxycarbonyl(carboethoxy), optionally substituted phenoxy-carbonyl such as phenoxy-carbonyl itself and chloro- or bromo-phenoxy-carbonyl, optionally substituted N-phenyl-carbamoyl such as N-phenyl-carbamoyl itself and N-anisyl-carbamoyl and N-tolyl-carbamoyl, lower alkyl-carbamoyl such as N-methyl, N-ethyl, N:N-dimethyl- and N:N-diethyl-carbamoyl, optionally substituted anilino such as anilino itself and anisidino, 25 toluidino and chloro- or bromo-anilino, lower alkylamino such as N-methyl-, N-n-propyl-, N:N-diethyl, and N-methyl-N-ethylamino, lower alkylsulphonyl such as methylsulphonyl, optionally substituted phenylsulphonyl such as phenylsulphonyl itself and *p*-tolylsulphonyl and *m*-nitrobenzenesulphonyl, radicals of the formula UCO— such as acetoxy, benzoyloxy and chlorobenzoyloxy, and UCONH— such as 35 acetylamino, propionylamino, benzoylamino and methoxybenzoylamino.

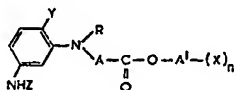
It is however preferred that *n* represents 1, so that A' represents an alkylene radical containing from 1 to 4 carbon atoms such as methylene, ethylene, propylene, trimethylene, 40 tetramethylene, and  $\alpha$ : $\beta$ -dimethylethylene.

According to a further feature of the invention there is provided a process for the manufacture of the water-insoluble monoazo dyestuffs of the invention which comprises diazotising an amine of the formula:—



Formula I

and coupling the resulting diazo compound with a coupling component of the formula:—



Formula II

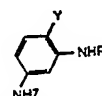
wherein W<sup>1</sup>, W<sup>2</sup>, A, A', R, X, Y, Z and *n* have the meanings stated above.

The process can be carried out by conventional methods, for example by dissolving the amine of Formula I in the nitrosylsulphuric acid at a temperature in the region of 10°—

25° C, and adding the resulting solution of the diazo compound to a solution of the coupling component in water containing a water-soluble organic liquid such as acetone and/or an inorganic acid such as hydrochloric acid. The pH of the mixture is then raised to effect coupling by the addition of sodium acetate and the resulting dyestuff is isolated by conventional methods.

As examples of the amines of Formula I there may be mentioned 2:4-dinitro-5-(chloro or bromo)-aniline, 2:4-dinitro-5-aminobenzonitrile, 2:4-dinitro-5-aminoacetanilide, 2:4:6-trinitroaniline, 2:4-dinitro-6-(chloro- or bromo)-aniline and 2:4-dinitro-6-cyanoaniline.

The coupling components of Formula II can be conveniently obtained by conventional methods, for example by condensing an amine of the formula:—

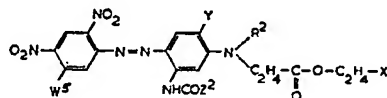


with one molecular proportion of a halogeno alkanic acid or acrylic acid and esterifying the resulting acid with an alcohol of the formula:—HO—A'—(X)<sub>n</sub>.

As specific examples of the said coupling components there may be mentioned 2-(methyl, methoxy or ethoxy)-5-acetylamino-N-(methyl or ethyl)-N-[ $\beta$ -( $\beta'$ -methoxyethoxycarbonyl)ethyl]aniline, 3-acetylamino-N-(methyl or ethyl)-N-[ $\beta$ -( $\beta'$ -phenoxyethoxycarbonyl)ethyl]aniline, 3-acetylamino-N-(methyl or ethyl)-N-[ $\beta$ -cyanomethoxycarbonyl-ethyl]aniline and 2-(methoxy or ethoxy)-5-(acetylamino or propionylamino)-N-(methyl or ethyl)-N-[ $\beta$ -( $\beta'$ -(acetoxy- or propionyloxy or methoxycarbonyl- or ethoxycarbonyl)-ethoxycarbonyl)ethyl]aniline.

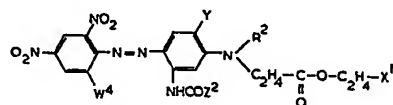
A preferred class of the dyestuffs of the invention comprises the dyestuffs wherein W<sup>2</sup> is a hydrogen atom, and W<sup>1</sup> is chlorine, bromine, cyano or an acylamino group of the formula:—NHZ<sup>1</sup> wherein Z<sup>1</sup> has the meaning stated.

A second preferred class of the monoazo dyestuffs of the invention comprises the monoazo dyestuffs of the formula:—



wherein Y has the meaning stated, R<sup>2</sup> is lower alkyl, Z<sup>2</sup> is lower alkyl, W<sup>3</sup> is chlorine, bromine, cyano or —NHCOZ<sup>2</sup>, and X<sup>1</sup> is cyano, lower alkoxy, lower alkoxy-carbonyl, carbamoyl, acetoxy, propionyloxy or butyryloxy.

A third preferred class of the monoazo dyestuffs of the invention comprises the monoazo dyestuffs of the formula:—



wherein Y has the meaning stated, R<sup>2</sup> is lower alkyl, Z<sup>2</sup> is hydrogen or lower alkyl, X' is cyano, lower alkoxy, lower alkoxy carbonyl, carbamoyl, acetoxy, propionyloxy or butyryloxy, and W<sup>4</sup> is chlorine, bromine, nitro or cyano.

The monoazo dyestuffs, as hereinbefore defined, are valuable for colouring synthetic textile materials, for example cellulose acetate and cellulose triacetate textile materials, polyamide textile materials such as polyhexamethylene-adipamide textile materials, and preferably aromatic polyester textile materials such as polyethylene terephthalate textile materials. Such textile materials can be in the form of thread, yarn, or woven or knitted fabric.

Such textile materials can conveniently be coloured with the monoazo dyestuffs, as hereinbefore defined, by immersing the textile material in a dyebath comprising an aqueous dispersion of one or more of the said dyestuffs, which dyebath preferably contains a non-ionic, cationic and/or non-ionic surface-active agent and thereafter heating the dyebath for a period at a suitable temperature. In the case of secondary cellulose acetate textile materials it is preferred to carry out the dyeing process at a temperature between 60° and 85° C; in the case of cellulose triacetate or polyamide textile materials it is preferred to carry out the dyeing process at 95° to 100° C; in the case of aromatic polyester textile materials the dyeing process can either be carried out at a temperature between 90° and 100° C, preferably in the presence of a carrier such as diphenyl or *o*-hydroxydiphenyl, or at a temperature above 100° C, preferably at a temperature between 120 and 140° C under superatmospheric pressure.

Alternatively the aqueous dispersion of the said monoazo dyestuff can be applied to the textile material by a padding or printing process, followed by heating or steaming of the textile material. In such processes it is preferred to incorporate a thickening agent, such as gum tragacanth, gum arabic or sodium alginate, into the aqueous dispersion of the said monoazo dyestuff.

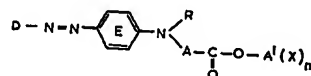
At the conclusion of the colouring process it is preferred to give the coloured textile material a rinse in water or a brief soaping treatment before finally drying the coloured textile material. In the case of aromatic polyester textile materials it is also preferred to subject the coloured textile material to a treatment in an alkaline aqueous solution of sodium hydrosulphite before the soaping in order to

remove loosely attached dyestuff from the surface of the textile material.

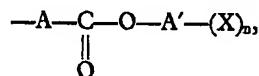
The monoazo dyestuffs have excellent affinity and build-up properties on synthetic materials, and in particular on aromatic polyester and acetate rayon textile materials, so enabling deep shades to be obtained. The resulting colorations have excellent fastness to light, to wet treatments, and, in particular, to dry heat treatments such as those carried out at high temperatures during pleating operations.

If desired the dyestuffs of the invention can be applied to synthetic textile materials in conjunction with other disperse dyes, such as are described in, for example, British Specification Nos. 806,271, 835,819, 840,903, 847,175, 852,396, 852,493, 859,899, 865,328, 872,204, 894,012, 908,656, 910,306, 913,856, 919,424, 944,513, 944,722, 953,887, 959,816, 960,235 and 961,412.

In British Specification No. 909,843 there are described and claimed the water-insoluble azo dyestuffs of the formula:—



wherein D represents a mono- or bi-cyclic aromatic nucleus, R stands for a lower alkyl or aralkyl group, either of which may carry substituents other than sulphonic and carboxylic acid radicals, or for the group



A represents a saturated di- or tri-valent aliphatic radical of from 1 to 4 carbon atoms, X represents a cyano, lower alkoxy, carbo (lower alkoxy), carbonamido, acyl, acyloxy, acylamino, amino, alkylamino, dialkylamino, or mono-cyclic aryl radical, n is 1 to 2, and the nuclei D and E may carry substituents other than sulphonic and carboxylic acid radicals.

Compared with the dyestuffs which are specifically described in Specification No. 909,843, the dyestuffs of the present invention give colorations on aromatic polyester textile materials which have a much higher fastness to dry heat treatments.

The invention is illustrated but not limited by the following Examples in which the parts are by weight:—

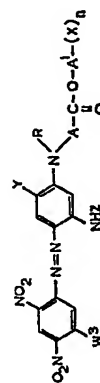
#### Example 1.

2.2 Parts of 2:4-dinitro-5-chloroaniline are added to nitrosylsulphuric acid, which is obtained by dissolving 0.7 parts of sodium nitrate in 8 parts of sulphuric acid monohydrate at 15° C., and the mixture is stirred for 2 hours at 10° C to 15° C. The Solution so obtained is added to a solution of 3.4 parts

- of 2-methoxy-5-acetylamino-N-ethyl-N- $[\beta$ -  
( $\beta'$ -methoxyethoxycarbonyl)ethyl]aniline in a  
mixture of 150 parts of water and 60 parts of  
acetone at 5° C., sodium acetate then being  
5 added to raise the pH to 4, and the mixture  
is stirred for 60 minutes. The dyestuff is then  
filtered off, stirred in an aqueous solution of  
sodium carbonate, and the precipitated dyestuff  
is filtered off, washed with water and dried.
- 10 When dispersed in aqueous medium the dye-  
stuff has excellent affinity for polyethylene  
terephthalate textile materials which it dyes in  
navy blue shades having excellent fastness to  
dry heat treatments, and to light.
- 15 The 2-methoxy-5-acetylamino-N-ethyl-N-  
 $[\beta$  - ( $\beta'$  - methoxyethoxycarbonyl)ethyl]aniline  
used in the above Example was obtained by  
condensing 2-methoxy-5-nitro-N-ethylaniline  
with acrylic acid, esterifying the resulting pro-  
duct with  $\beta$ -methoxyethanol in sulphuric acid,  
20 reducing the nitro group to an amino group  
and finally acylating this using one molecular  
proportion of acetic anhydride in pyridine at  
20° C.
- Example 2. 25
- In place of the 2.2 parts of 2:4-dinitro-5-  
chloroaniline used in Example 1 there are used  
2.4 parts of 2:4-dinitro-5-aminoacetanilide or  
2.62 parts of 2:4-dinitro-6-bromoaniline  
whereby dyestuffs are obtained which dye 30  
aromatic polyester textile materials in  
greenish-blue shades having excellent fastness  
to dry heat treatments and to light.
- The following Table gives further Examples  
of the dyestuffs of the invention which are ob- 35  
tained by diazotising the amines listed in the  
second column of the Table and coupling the  
resulting diazo compounds with the coupling  
components listed in the third column of the  
Table using methods similar to that described 40  
in Example 1. The fourth column of the Table  
gives the shades obtained when the dyestuffs  
are applied to polyester textile materials.

Example	Amine	Coupling Component	Shade
3	2:4-dinitro-6-chloroaniline	2-methoxy-5-acetylamino-N-ethyl-N-[β-(β'-methoxyethoxycarbonyl)ethyl]aniline	Navy Blue
4	2:4:6-trinitroaniline	"	Bluish-green
5	2:4-dinitro-6-cyanoaniline	"	"
6	2:4-dinitro-6-bromoaniline	2-ethoxy-5-acetylamino-N-ethyl-N-[β-(β'-methoxyethoxycarbonyl)ethyl]aniline	Greenish-blue
7	"	2-methoxy-5-acetylamino-N- <i>n</i> -propyl-N-[β-(β'-methoxyethoxycarbonyl)ethyl]aniline	"
8	"	2-methoxy-5-acetylamino-N- <i>n</i> -butyl-N-[β-(β'-methoxyethoxycarbonyl)ethyl]aniline	"
9	2:4-dinitro-6-bromoaniline	2-methoxy-5-acetylamino-N-ethyl-N-[β-(β'-ethoxyethoxycarbonyl)ethyl]aniline	Greenish-blue
10	2:4-dinitro-6-cyanoaniline	3-acetylamino-N-ethyl-N-[β-(β'-methoxyethoxycarbonyl)ethyl]aniline	"

The following Table gives further Example of the water-insoluble monazo dyestuffs of the invention having the formula: —

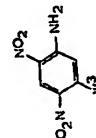


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the symbols of which have the values given in the respective columns of the Table, and the shades of the dyeings obtained from the said dyestuffs are given in the last column of the Table.

10

The said dyestuffs may be obtained by methods similar to that described in Example I by diazotising the appropriate amines of the formula: —



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and coupling the resulting diazo compounds with the appropriate coupling components of Formula II.

Example	W <sup>3</sup>	Z	Y	A	A'	X	n	R	Shade
11	bromine	acetyl	methoxy	ethylene	ethylene	methoxy	1	ethyl	navy blue
12	cyano	"	"	"	"	"	1	"	"
13	$\beta$ -chloropropionylamino	propionyl	ethoxy	"	"	ethoxy	1	"	greenish blue
14	methylsulphonylamino	"	"	"	"	"	1	"	navy blue
15	chlorine	"	hydrogen	$\beta$ -methyl-ethylene	ethylene	propionyloxy	1	methyl	violet
16	"	"	methoxy	ethylene	"	cyano	1	ethyl	navy blue
17	"	"	"	"	methylidyne	"	2	"	"
18	"	"	"	ethylene	ethylene	benzoyl	1	"	"
19	"	"	"	"	"	methoxycarbonyl	1	"	"
20	"	"	"	"	methylidyne	ethoxycarbonyl	2	"	"
21	"	"	"	"	ethylene	butoxycarbonyl	1	"	"
22	"	carboethoxy	"	"	"	methoxy	1	"	"

Example	W <sup>a</sup>	Z	Y	A	A'	X	n	R	Shade
23	chlorine	$\beta$ -chloropropionyl	methoxy	ethylene	ethylene	methoxy	1	ethyl	navy blue
24	"	<i>p</i> -toluenesulphonyl	"	"	"	"	1	"	"
25	bromine	carbamoyl	ethoxy	"	trimethylene	"	1	<i>n</i> -propyl	greenish blue
26	chlorine	acetyl	methoxy	"	"	methoxy	1	phenyl	reddish navy blue
27	"	benzoyl	"	"	"	"	1	ethyl	navy blue
28	"	<i>o</i> -chlorobenzoyl	"	"	"	"	1	"	"
29	"	$\beta$ -bromopropionyl	"	"	"	"	1	"	"
30	"	$\gamma$ -methoxybutyryl	"	"	"	"	1	"	"
31	"	acetyl	methoxy	ethylene	$\beta$ -methyl-ethylene	cyano	1	ethyl	navy blue
32	"	"	"	"	"	acetyl	1	ethyl	"
33	"	"	"	"	"	phenoxy	1	"	"

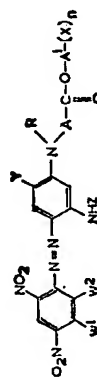
Example	W <sup>s</sup>	Z	Y	A	A'	X	n	R	Shade
34	chlorine	acetyl	methoxy	ethylene	ethylene	<i>p</i> -nitrophenoxy	1	ethyl	navy blue
35	"	"	"	"	"	hydroxy	1	"	"
36	"	"	"	"	"	chlorine	1	"	"
37	"	"	"	"	"	bromine	1	"	"
38	"	"	"	"	"	<i>m</i> -chlorophen- oxy carbonyl	1	"	"
39	"	"	"	"	"	N-ethyl car- bamoyl	1	"	"
40	"	"	"	"	"	N-phenyl car- bamoyl	1	"	"
41	"	"	"	"	"	carbamoyl	1	n-butyl	"
42	"	"	"	"	"	anilino	1	methyl	Reddish blue
43	"	"	"	"	"	ethylsulphonyl	1	n-butyl	navy blue
44	"	"	"	"	"	<i>p</i> -toluenesul- phonyl	1	ethyl	"
45	"	"	"	"	"	acetylamino	1	"	"
46	"	"	"	"	"	benzoylamino	1	"	"



Example	W <sup>3</sup>	Z	Y	A	A'	X	n	R	Shade
47	chlorine	acetyl	hydrogen	ethylene	ethylene	methoxy	1	isopropyl	violet
48	"	"	methoxy	"	"	"	1	$\beta$ -hydroxyethyl	navy blue
49	"	"	"	"	"	"	1	$\gamma$ -methoxypropyl	"
50	"	"	"	"	"	"	1	$\beta$ -phenoxyethyl	navy blue
51	"	"	"	"	"	"	1	$\beta$ -acetoxylethyl	"
52	"	"	"	"	"	"	1	$\beta$ -( $\beta'$ -acetoxyethoxy)ethyl	"
53	"	"	"	"	"	"	1	$\gamma$ -chloro- $\beta$ -hydroxypropyl	"
54	"	"	"	"	"	"	1	$\beta$ -ethoxycarbonyl ethyl	"

# WHAT WE CLAIM IS:—

1. The water-insoluble monoazo dyestuffs, free from sulphonie and carboxylic acid groups, which are of the formula:—



wherein W<sup>1</sup> is hydrogen, chlorine, bromine, cyano or an acylamino group of the formula NHZ<sup>1</sup> and W<sup>2</sup> is hydrogen, chlorine, bromine, cyano or nitro, provided that one, but not

both, of W<sup>1</sup> and W<sup>2</sup> is hydrogen; Z and Z<sup>1</sup> each independently represents an acyl group of the formula —COV or —SO<sub>2</sub>U; V is an amino group or a lower alkyl, lower alkoxy, phenyl or phenoxy radical which can contain substituents; U is a lower alkyl or phenyl radical which can contain substituents; Y is hydrogen, lower alkyl or lower alkoxy;

R is lower alkyl hydroxy lower alkyl, lower alkoxy lower alkyl, aryl lower alkyl,  $\beta$ -phenoxyethyl,  $\beta$ -acetoxylethyl,  $\beta$ -( $\beta'$ -acetoxyethoxy)ethyl,  $\gamma$ -chloro- $\beta$ -hydroxypropyl,  $\beta$ -ethoxycarbonyl ethyl or optionally substituted phenyl;

A is an alkylene radical containing from 1

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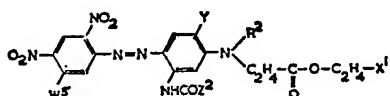
to 6 carbon atoms having not more than two carbon atoms between the nitrogen atom N and the carbonyl group;

$n$  is 1 or 2, and A' represents a di- or tri-valent alkane radical, depending on the value of  $n$ , containing up to 4 carbon atoms;

and X is cyano, lower alkoxy, optionally substituted phenoxy, hydroxy, chlorine, bromine, lower alkoxycarbonyl, optionally substituted phoxycarbonyl, carbamoyl, optionally substituted N-phenylcarbamoyl, N-lower alkyl or N:N-di lower alkyl carbamoyl amino, optionally substituted anilino, N-lower alkyl-amino, N:N-di lower alkylamino, lower alkyl-sulphonyl, optionally substituted phenylsulphonyl or a radical of the formula  $\text{U.CO—}$ ,  $\text{U.CO—}$  or  $\text{U.CONH—}$ .

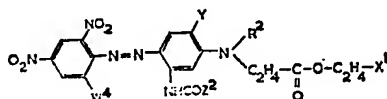
2. The water-insoluble monoazo dyestuffs as claimed in Claim 1 wherein  $\text{W}^2$  is a hydrogen atom and  $\text{W}^1$  is chlorine, bromine, cyano or an acylamino group of the formula  $\text{—NHZ}^1$  wherein  $\text{Z}^1$  has the meaning stated in Claim 1.

3. The water-insoluble monoazo dyestuffs as claimed in Claims 1 or 2 which are of the formula:—



wherein Y has the meaning stated in Claim 1,  $\text{R}^2$  is lower alkyl,  $\text{Z}^2$  is lower alkyl,  $\text{W}^5$  is chlorine, bromine, cyano or  $\text{—NHCOZ}^2$ , and  $\text{X}^1$  is cyano, lower alkoxy, lower alkoxycarbonyl, carbamoyl, acetoxy, propionyloxy or butyryloxy.

4. The water-insoluble monoazo dyestuffs as claimed in Claim 1 which are of the formula:—

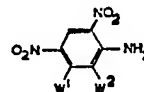


wherein Y has the meaning stated in Claim 1,

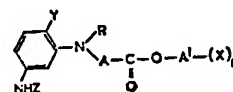
$\text{R}^2$ ,  $\text{Z}^2$  and  $\text{X}^1$  have the meanings stated in Claim 3, and  $\text{W}^4$  is chlorine, bromine, nitro or cyano.

5. Water-insoluble monoazo dyestuffs as claimed in any of Claims 1 to 4 as hereinbefore described especially with reference to any of the Examples.

6. Process for the manufacture of the water-insoluble monoazo dyestuffs as claimed in Claim 1 which comprises diazotising an amine of the formula:—



and coupling the resulting diazo compound with a coupling component of the formula:—



wherein  $\text{W}^1$ ,  $\text{W}^2$ , A, A', R, X, Y, Z and  $n$  have the meanings stated in Claim 1.

7. Process as claimed in Claim 6 wherein  $\text{W}^2$  is a hydrogen atom and  $\text{W}^1$  is chlorine, bromine, cyano or an acylamino group of the formula  $\text{—NHZ}^1$  wherein  $\text{Z}^1$  has the meaning stated in Claim 1.

8. Process for the manufacture of water-insoluble monoazo dyestuffs as claimed in any of Claims 1 to 5 as hereinbefore described especially with reference to any of the Examples.

9. Process for colouring synthetic textile materials which comprises applying to the textile material by a dyeing, padding or printing process an aqueous dispersion of a dyestuff as claimed in any of Claims 1 to 5.

10. Process as claimed in Claim 9 wherein the textile material is an aromatic polyester textile material.

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